

Table 3-2. C-Site Measurements

	<u># days</u>	<u>Time duration</u>	<u>Analytical Method</u>
O <sub>3</sub>	all	hourly	UV absorption
NO	all	" "	Chemiluminescence
NO <sub>x</sub>	all	" "	Chemiluminescence
CO	all	" "	NDIR
SO <sub>2</sub>	all	" "	Pulsed fluorescence
Wind speed	all	" "	Cup anemometer
Wind direction	all	" "	Wind vane
Total suspended particles	6th day	24 hrs	HiVol sampler
PM-10	6th day	24 hrs	HiVol with Size Selective Inlet
Tracer Samplers (selected sites)	all tracer days	1 hr integration	Automated bag or syringe samplers

Table 3-3a. Network Measurements at B-Sites  
(See Table 3-3f for abbreviations)

Observable	Dur- ation	No. per site-day	Meas. method	Ambient concentrations typical range	Units*	Lower quantifiable limit	Precision**	Reason for selection	References and notes
<b>METEOROLOGY</b>									
Wind speed	Cont.	24	Cup anemometer	3	m/sec	0.25	0.25	A	
Wind direction	Cont.	24	Vane	IA	degrees	IA	3	A	
Temperature	Cont.	24	Thermistor	IA	degrees C	IA	0.5	A	
Dew point	Cont.	24	Dew cell	IA	degrees C	IA	0.5	A	
UV radiation	Cont.	24	UV radiometer	30	watts/m <sup>2</sup>	0.5	0.25	A	
<b>GASES (continuous)</b>									
O <sub>3</sub>	Cont.	24	UV absorption	30	ppb	2	15%	A	
NO	Cont.	24	Chemiluminescence	30	ppb	2	15%	A	
NO <sub>x</sub>	Cont.	24	Chemiluminescence	50	ppb	2	15%	A	
SO <sub>2</sub>	Cont.	24	Pulsed fluorescence	6	ppb	2	15%	A	
CO	Cont.	24	NDIR	2	ppm	0.5	15%	A	
<b>GASES (integrated sample)</b>									
SO <sub>2</sub> in the	4 to 7 hr.	5	Impreg. filter	6	ppb	0.2	7%	C,E	1
NH <sub>3</sub> SCAQS	4 to 7 hr.	5	Denuder tube	5	ppb	0.3	10%	D	2
HNO <sub>3</sub> Sampler	4 to 7 hr.	5	Denuder diff & Nylon	7	ppb	0.4	10%	D	3
Carbonyls	1 hr.	3	DNPH absorber	3-7	1 to 30 (HCHO)	0.5	10%	C	4
C1-C10 HC	1 hr.	3	Canisters and GC/FID	0.1 to 50	ppbC	0.1	10%	B	5
PAN	1 hr.	24	In-situ GC/EC	5-10	ppb	0.5	15%	C	6
H2O2†	1 to 7 hr.	8	POHPAA fluorescence	5 (est.)	ppb	0.5	3%	C	7
<b>AEROSOL PHYSICAL PROPERTIES</b>									
Size dist.††	Cont.	24	OPC(Climet 208, PMS ASAP-X)	IA	IA	IA	Resolves diameter ratio of 1.8	B	8
Size dist.††	Cont.	24	EAA	IA	IA	IA	10	E,F	8
Light scattering	Cont.	24	Integrating nephelometer	350	Mm-1	10	10%	B	9
Data acquisition	Cont.	--	Micro-computer	IA	IA	IA	5mV for 10V f.s.	G	10
<b>AEROSOL CHEMISTRY (in the SCAQS Sampler)</b>									
PM-10/PM-2.5:	4 to 7 hr.	5	SA-254/Bendix 240	40	µg/m <sup>3</sup>	5.8	7%	B	11
Mass	4 to 7 hr.	5	Gravimetric	5	µg/m <sup>3</sup>	0.06	7%	B	
SO <sub>4</sub> =	4 to 7 hr.	5	IC	8	µg/m <sup>3</sup>	0.09	7%	B	
NO <sub>3</sub> -	4 to 7 hr.	5	IC	3	µg/m <sup>3</sup>	0.1	7%	B	
Cl-	4 to 7 hr.	5	AC	5	µg/m <sup>3</sup>	0.05	7%	B	
NH <sub>4</sub> +	4 to 7 hr.	5	WDXRF	2.5	ng/m <sup>3</sup>	See Table 3-3b	5 to 20%	B,G,H	
Elements	4 to 7 hr.	5	Thermal combustion	20	µg/m <sup>3</sup>	0.08	10 to 25%	D	
Elemental C	4 to 7 hr.	5	Thermal combustion	20	µg/m <sup>3</sup>	1.5	10 to 25%	D	
Organic C	4 to 7 hr.	5	LASER int. plate on Nuclepore	50	µg/m <sup>3</sup>	5.8	7%	C,G	12
Fine Babs	4 to 7 hr.	5	SA-321A, quartz filt.	5	µg/m <sup>3</sup>	0.06	7%	A	
PM-10	24 hr.	1	Gravimetric	8	µg/m <sup>3</sup>	0.09	7%	A	
Mass	24 hr.	1	IC	5	µg/m <sup>3</sup>	0.06	7%	A	
SO <sub>4</sub> =	24 hr.	1	AC	5	µg/m <sup>3</sup>	0.06	7%	A	
NO <sub>3</sub> -	24 hr.	1	AC	8	µg/m <sup>3</sup>	0.09	7%	A	
<b>AEROSOL SIZE RESOLVED CHEMISTRY††</b>									
SO <sub>4</sub> =	4 to 12 hr.	4	Berner LPI & IC	2	µg/m <sup>3</sup>	0.4***	7%	D	
NO <sub>3</sub> -	4 to 12 hr.	4	Berner LPI & IC	2	µg/m <sup>3</sup>	0.8***	7%	D	
Cl-	4 to 12 hr.	4	Berner LPI & IC	2	µg/m <sup>3</sup>	0.8***	7%	D	
H+	4 to 12 hr.	4	Berner LPI & electrode	NA	µg/m <sup>3</sup>	NA	NA	D	
NH <sub>4</sub> +	4 to 12 hr.	4	Berner LPI & AC	2	µg/m <sup>3</sup>	0.8***	7%	D	
Na+K+	4 to 12 hr.	4	Berner LPI & IC	2	µg/m <sup>3</sup>	0.08***	7%	D	
Elemental carbon	4 to 12 hr.	4	MOUDI & therm. comb.	0.5	µg/m <sup>3</sup>	0.2 to 4	10 to 25%	D	13
Organic carbon	4 to 12 hr.	4	MOUDI & therm. comb.	1.5	µg/m <sup>3</sup>	0.2***	10 to 25%	D	
Elements	4 to 7 hr.	5	DRUM & PIXE	1.5	ng/m <sup>3</sup>	Similar to Table 3-3b	5 to 20%	B,F	14

\* Units apply to both ambient concentrations and the lower quantifiable limit.

†† Precision for values well above the lower quantifiable limit.

\*\*\* µg/m<sup>3</sup> per stage

† Measurements made only at Claremont, Downtown L.A., Long Beach, and Rubidoux.  
†† Measurements made only at Claremont, Long Beach, and Rubidoux.

Table 3-3b. Lower Quantifiable Limits for EPA's Wavelength Dispersive X-ray Fluorescence Analysis of Aerosol Deposits on Teflon Membrane Filters.

Element symbol	Lower Quantifiable Limit (ng/m <sup>3</sup> )*
Na	91
Mg	5
Al	7
Si	8
P	3
S	12
Cl	5
K	5
Ca	10
Ti	5
V	8
Cr	58
Mn	12
Fe	25
Ni	14
Cu	25
Zn	12
As	19
Se	27
Br	24
Sr	49
Mo	117
Cd	2
Ba	7
Hg	52
Pb	96

\*Assumes 34 lpm flow for 4 hrs. through 47 mm diameter filter. Detection limits are twice the standard deviation of several blank filter background spectra. Excitation is with: Cr anode, 54 KeV, 46 ma, 30mm diameter analysis area, and 20 to 100 sec. count times.

Table 3-3c. C<sub>1</sub> to C<sub>10</sub> Hydrocarbons  
Measured by GC/FID

---

Ethane	2,4-Dimethylpentane
Ethylene	Benzene
Acetylene	Cyclohexane
Propane	2,3-Dimethylpentane
Propene	3-Methylhexane
i-Butane	2,2,3-Trimethylpentane
i-Butane	n-Heptane
1-Butene	Methylcyclohexane
n-Butane	2,4-Dimethylhexane
trans-2-Butene	2,3,4-Trimethylpentane
2,2-Dimethylpropane	Toluene
cis-2-Butene	2,3-Dimethylhexane
3-Methyl-1-butene	2-Methylheptane
i-Pentane	3-Ethylhexane
1-Pentene	n-Octane
2-Methyl-1-butene	Ethylcyclohexane
n-Pentane	Ethylbenzene
Isoprene	p-Xylene
trans-2-Pentene	m-Xylene
cis-2-Pentene	Styrene
2-Methyl-2-butene	o-Xylene
2,2-Dimethylbutane	n-Nonane
Cyclopentene	$\alpha$ -Pinene
4-Methyl-1-pentene	i-Propylbenzene
Cyclopentane	n-Propylbenzene
2,3-Dimethylbutane	3-Ethyltoluene
2-Methylpentane	2-Ethyltoluene
3-Methylpentane	1,3,5-Trimethylbenzene
2-Methyl-1-pentene	1-Ethyltoluene
1-Hexene	$\beta$ -Pinene
n-Hexane	Myrcene
trans-2-Hexene	1,2,4-Trimethylbenzene &
1,3,5-Trimethylbenzene	sec-Butylbenzene
1,2,4-Trimethylbenzene	$\Delta^3$ -Carene
cis-2-Hexene	$\alpha$ -Terpinene
Methylcyclopentane	d-Limonene
	$\gamma$ -Terpinene
	Terpinolene

---

Table 3-3d. Key to Reasons for Selection.

- 
- |   |   |
|---|---|
| A | Already available at the B-sites.   |
| B | Method in general use because of its sensitivity, accuracy and relative freedom from interferences. Accuracy and precision have been evaluated with field data. |
| C | Only method available with adequate sensitivity.  |
| D | ARB Nitrogen and Carbeneous Species Methods Comparison Studies showed consistent results.   |
| E | Method has been evaluated in previous field studies.  |
| F | Equipment cost-effectively available.   |
| G | Other criteria being equal, initial and operating costs are minimized.  |
| H | Method to be provided by a sponsor.   |
-

Table 3-3e. References and Notes.

- 
1.  $\text{Na}_2\text{CO}_3$ /glycerine impregnated Whatman 541 cellulose fiber filter for sulfur dioxide. The lower quantifiable limit is small and the method has been characterized (Forrest et al., 1981) and used in the field.
  2. Oxalic acid coated denuder tube with backup filter impregnated with oxalic acid (Ferm, 1979).
  3.  $\text{MgO}$ -coated denuder difference method for nitric acid (Appel, Tokiwa, and Haik, 1981).
  4. 2,4-dinitrophenylhydrazine (DNPH) absorbing cartridge for carbonyls (Levin et al., 1985; Fung and Grosjean, 1982).
  5. Hydrocarbons are pumped into canisters for later laboratory analysis by GC/FID. There is less adsorption and desorption of hydrocarbons in electropolished stainless steel canisters than in bags (Grosjean and Fung, 1984).
  6. Electron capture gas chromatography (EC-GC) for PAN (Stephens, 1969b). Units are calibrated and operated continuously in the field.
  7. Para-hydroxy phenylacetic acid - horseradish peroxidase method for gas phase hydrogen peroxide (Lazrus et al., 1986; Kok et al., 1986; Heikes et al., 1985). Samples are collected in bubblers.
  8. Climet optical particle counter, PMS ASASP-X, and electrical aerosol analyzer (EAA) determine aerosol size distribution data in the 1 to  $10\text{ }\mu\text{m}$ ,  $.09$  to  $3\text{ }\mu\text{m}$ , and  $0.003$  to  $1\text{ }\mu\text{m}$  size ranges, respectively.
  9. Integrating nephelometer measures scattering of light by particles.
  10. Microcomputer data acquisition system. Flexible and cost effective. Data can be recorded in a format which can be read by most laboratories, so adding data from other experiments is possible.
  11. A specially designed aerosol sampling system has been constructed for SCAQS. The SA-254 size selective inlet is for  $<10\text{ }\mu\text{m}$  particles (Olin and Bohn, 1983) and the Bendix 240 cyclone is for  $<2.5\text{ }\mu\text{m}$  particles (Chan and Lippman, 1977) at  $113\text{ l/min}$  flow rates.
  12. Hi vol sampler with SA-321A  $10\text{ }\mu\text{m}$  inlet. This inlet may pass some large particles.
  13. The MOUDI Impactor (Marple and Rubow, 1984) collects submicron particles in defined size ranges on aluminum foils for subsequent carbon analysis.
  14. The DRUM Impactor acquires submicron-sized samples on mylar films which are submitted to PIXE analysis.
-

Table 3-3f. Key to Abbreviations.

---

AA	- Atomic Absorption Spectroscopy
AC	- Automated Colorimetry
Bendix 240	- Cyclone with 2.5 $\mu\text{m}$ cut-point at 113 l/min flow rate
DNPH	- 2,4 dinitrophenylhydrazine
DRUM	- Davis Rotating Universal Multistage Impactor
EAA	- Electrical Aerosol Analyzer
GC/EC	- Gas Chromatography with Electron Capture Detection
GC/FID	- Gas Chromatography with Flame Ionization Detection
IA	- Inapplicable
IC	- Ion Chromatography
LPI	- Low Pressure Impactor
MOUDI	- Multi-Orifice Uniform Deposit Impactor
NA	- Not Available
NDIR	- Non-Dispersive Infrared Absorption
OPC	- Optical Particle Counter
PIXE	- Proton-Induced X-ray Emission Spectroscopy
SA-254	- Sierra Andersen size-selective inlet with 10 $\mu\text{m}$ cut-point at 113 l/min.
SA-321A	- Sierra Andersen two-stage size-selective inlet with 10 $\mu\text{m}$ cut-point at 1130 l/min.
WDXRF	- Wavelength Dispersive X-ray Fluorescence

---

samples to match the every sixth-day 24 hour PM-10 samples, which are changed at midnight standard time year round. Carbonyl absorbers and hydrocarbon canisters will collect one hour samples starting at 0700, 1200, and 1600 local time; and hydrogen peroxide samples will correspond to the particle sampling schedule except that hourly samples will be taken from 1400 to 1800. High volume PM-10 samples will be of 24-hour duration and will be changed at midnight. MOUDI and Berner LPI samples will be changed at 0600, 1000, 1400, and 1800. The sample durations and changing times have been selected as a compromise between: 1) the amount of time needed to obtain a detectable deposit, 2) minimizing the number of samples to reduce costs, 3) manpower deployment among the different instruments, 4) correspondence of measurement periods, and 5) temporal resolution required for modeling and data interpretation. Though the schedule cited above is not perfect, it is a reasonable compromise between these five requirements.

The B-site stations can be operated by one trained technician. For intensive study days, two technicians working overtime will operate the stations continuously. Having the stations manned full time will enable immediate identification of problems and rapid correction. In addition, it removes the requirement for automatic sequencing of filter sample devices. The technicians will primarily perform the routine station operations and will not be responsible for repairs. A separate, highly knowledgeable technician will be on call for repairs, and spares for critical components will be available at a central location.

A data acquisition system is included in Table 3-3a under the Aerosol Physical Property heading. A personal computer-based system has been designed to control the aerosol equipment and to record all continuous data.

A simplified flow diagram of the SCAQS Sampler is shown in Figure 3-5. This sampler has been designed to meet the specific requirements of SCAQS for integrated fine- and coarse-particle chemistry measurements and coordinated gas-phase measurements of low-level ammonia, sulfur dioxide and nitric acid. The sampler has also been designed to make it easy for the technician to change media for sequential samples and to document all necessary parameters for each sample. Two sets of sampling cassettes will be available at each site so that the technicians can load cassettes between sampling periods and can quickly switch cassettes at sample change times. The cassettes and media holders used for sampling and transport are all color coded, and an extensive media documentation scheme has been developed to minimize problems from sample handling errors.

#### A-Site Measurements

The primary measurements planned for the A-sites during the summer are summarized in Tables 3-4a through 3-4c. The fall A-site measurements will be finalized later. Many of the measurements listed are quite experimental in nature and are really special studies in themselves. Some of the measurement methods indicated in the table are unique to one investigator or group. Table 3-4a is organized in the same fashion as Table 3-3a for the B-sites, except that ambient concentrations, lower quantifiable limits, and precision are not included, since most of the techniques are still experimental. The measurements listed in Table 3-4 were suggested by the sponsors and technical reviewers and were refined to reflect the consensus of SCAQS participants. The



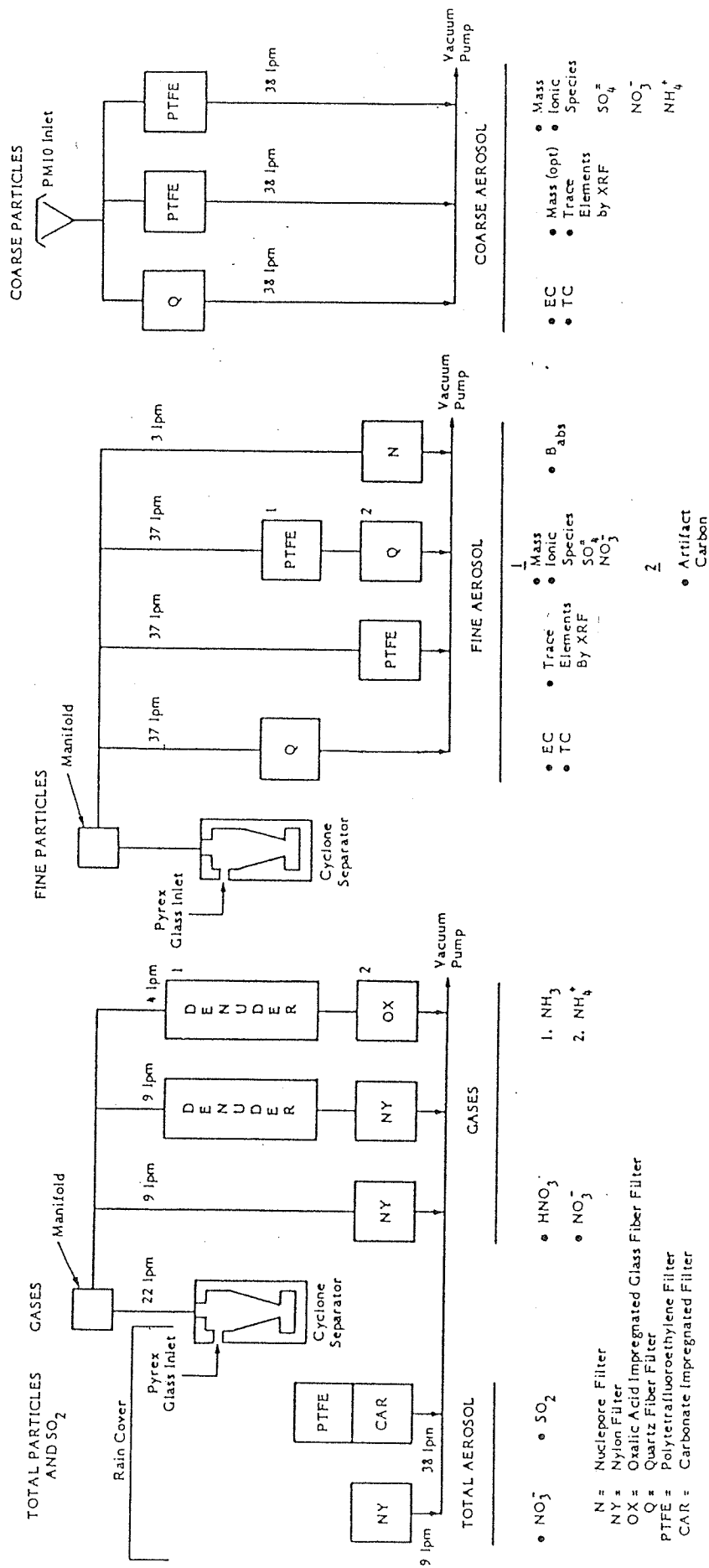


Figure 3-5. SCAQS Sampler for Gas and Size-Selective Aerosol Sampling.

Table 3-4a. Additional Measurements at A-Sites During the Summer  
(See Table 3-4b for abbreviations)

6/6/87

Observable	Dur- ation	No. per site-day	Site(s)*	Potential meas. method	Reason for Selection
<b>GASES</b>					
C1-C10 HC	1 hr.	3 more, 6 total	C, LB	Canister & GC/FID	A
C2-C12 HC	3 hr.	1; 2	LB, LA; C	Canister & GC/FID	E
Halocarbons	6 hr.	4	C	GC/EC	E
Carbonyls	1 hr.	3 more, 6 total	C, LB	DNPH absorber	A
Carbonyls	3 hr.	1; 2	LB, LA; C	DNPH absorber	A
Methyl & ethyl alcohol	4 to 7 hr.	5	C, LB	Charcoal absorber/thermal/impinger/GC-EC	E
Formic, acetic acid	4 hr.	6	C	Impreg. filter - IC	E
HONO, HCHO, NO2	15 min.	80	C, LB	DOAS	B,C,F
HNO3	4 to 7 hr.	5	C	DDMIC, TFR/IC, luminol detection	E
H2O2, HNO3	Cont.	24	C	TDLAS	B,E
PAN, NO2	4/hr.	24	C	GC/luminol	E
HNO3, HNO2	4 to 7 hr.	5	C	Annular denuder, IC	E
<b>RADICALS</b>					
NO3	15 min.	15	C, LB	DOAS	C
RO	Cont.	24	C	Chem. amplifier	E,F
<b>ORGANIC AEROSOL</b>					
EC, OC	2 hr.	12	C	Filter & thermal-optical	F
Carbon 14 (PM-2.5)	24 hr.	1**	C, LB, R	Accelerator mass spec.	E
Carbon 14 (PM-10)	24 hr.	1***	C, LB	Accelerator mass spec.	E
Organics	4 to 7 hr.	5	C	LPI & FTIR	E
<b>INORGANIC AEROSOL</b>					
Water			C, R	TDMA; heated nephelometer	E
Acidity, SO4=	4 to 7 hr.	5	C	Titration & IC	E
S speciation	Cont.	24	LB	Thermal/NH3 & FID	E
SO4=, NO3-	4 to 7 hr.	5	C	Annular denuder & IC	E
PM-10 ions	12	2	C	AC, AA	E
Br, Pb	5 hr.	1	C	WDXRF	E
Elements; EC, OC; SO4=, NO3-	4 to 7 hr.	5	C	Dicots & WDXRF; thermal combustion; IC	C,E
SO4=, NO3-	15 min.	3	C	LPI & flash vapor./FPD, IC	E
Elements	4 to 7 hr.	5	C, LB, R	IMPROVE & PIXE	E,F
Dry deposition	12 hr. +	2	C	IC on surrogate surfaces & vegetation	E
Coarse mass; SO4=, NO3-	24 hr.	1	C	Deposition plate/gravimetric; IC	E
Coarse mass; SO4=, NO3-	4 to 7 hr.	5	C	Rotary impactor/gravimetric; IC	E
<b>AEROSOL PHYSICAL PROPERTIES</b>					
Light absorption	Cont.	24	C	Spectrophone	E
Light absorption	4 hr.	6	C	Filter reflectance	E,F
Light absorption, abs. vs. RH	Cont.	24	C	Filter transmission (Aethalometer)	E,F
Path transmittance & radiance	Cont.	13	C	Radiance difference	E
Light extinction	Cont.	13	C	Telephotometer	E
Size vs. RH, vs. reactive gas	15 min.	3	C	TDMA	E,F
Light scattering vs. RH	15 min.	3	C, R	Heated nephelometer	E,F
Detailed fine part. size distribution			C	Electrical classifier	E
<b>INDIVIDUAL PARTICLES</b>					
Size & chem. comp.				Electron microscopy; microprobe; GC/MS	C,F
<b>OTHER</b>					
Mutagens	24 hr.	1	C		E
Toxic air contaminants	24 hr.	1	C, LB, LA, R	Canister & Tedlar bags- GC/FID	E
Calif. Dry Deposition Sampler	12 hr.	2	C		E
Operational Evaluation Network Sampler	12 hr.	2	C		E

\*For sites, C is Claremont, LB is Long Beach, LA is Los Angeles, R is Rubidoux.

\*\*Analyze only 24 of 36 samples.

\*\*\*Analyze only 7 of 24 samples.

Table 3-4b. Abbreviations for Analytical Methods

---

AA	- Atomic Absorption Spectroscopy
AC	- Automated Colorimetry
DDM	- Denuder Difference Method
DNPH	- 2,4 Dinitrophenylhydrazine
DOAS	- Differential Optical Absorption Spectroscopy
EC	- Elemental Carbon
FPD	- Flame Photometric Detector
FTIR	- Fourier Transform Infrared Spectroscopy
GC/EC	- Gas Chromatography with Electron Capture Detector
GC/FID	- Gas Chromatography with Flame Ionization Detector
GC/Luminol	- Gas Chromatography with Luminol Detector
GC/MS	- Gas Chromatography/Mass Spectroscopy
IC	- Ion Chromatography
LPI	- Low Pressure Impactor
OC	- Organic Carbon
PIXE	- Proton-Induced X-ray Emission Spectroscopy
TDLAS	- Tunable Diode Laser Absorption Spectroscopy
TDMA	- Tandem Differential Mobility Analyzer
WDXRF	- Wavelength Dispersive X-ray Fluorescence

---

Table 3-4c. Key to Reasons for Selection

---

A	Extension of measurements already made at B-sites.
B	This species also measured by instrument chosen to measure another species.
C	Method has adequate sensitivity, accuracy, freedom from interferences.
D	To increase the variety of elements determined.
E	Method provided by a sponsor.
F	Equipment availability.

---

criteria for selection of measurement methods were similar to those for the B-sites, even though many of the methods are quite experimental. Most A-site measurements will be made by individual investigators.

Since the A-sites are collocated with B-sites, the B-site measurements from Table 3-3 will also be performed at the A-sites. Two of the A-site measurements will be augmented. Three extra one hour C<sub>1</sub>-C<sub>10</sub> hydrocarbon and carbonyl samples will be obtained each day. The six total sets of samples will be collected starting at 0500, 0700, 0900, 1200, 1400, and 1600 local time on intensive study days.

In addition to the measurements listed in Table 3-4, many investigators are planning studies which are complementary to the primary SCAQS measurements and which will be located at the A-sites. A list of participants which includes those investigators identified by May 8, 1987 is included in Appendix A.

#### Complementary Toxic Air Contaminants Measurements

Toxic air contaminants will be measured at four SCAQS sites (Claremont, Long Beach, Los Angeles, and Rubidoux) during the summer field intensives. Two of these sites (Los Angeles and Rubidoux) are part of the ARB toxic network. These 24-hour samples will be taken in both stainless steel canisters and in tedlar bags. The compounds which will be measured are listed in Table 3-5. Also included as part of this project are replicate samples for analysis by multiple groups and an exchange of toxic gas standards.

### **3.5 AIRBORNE AIR QUALITY AND LIDAR MEASUREMENTS**

Airborne measurements are required to determine the pollutant distributions in the vertical dimension. They are especially important for documenting initial and boundary conditions, pollutant carryover, mixing layer height, representativeness of surface measurements, and nighttime chemistry aloft.

During the summer, two aircraft will be operated during the intensive study days. The spiral aircraft will measure the three dimensional pollutant distribution in the Basin. It will be instrumented with continuous fast response monitoring equipment, as shown in the top of Table 3-6. It will perform three flights per day, in early morning (0500-0800 PDT), mid-day (1000-1300 PDT), and afternoon (1500-1800 PDT). Its flight pattern will include vertical spirals at Burbank, El Monte, Fullerton, Hawthorne, Riverside, Upland, and offshore. The flights will take about 2.5 to 3 hours.

The orbit aircraft will be used in the summer to obtain integrated samples for later chemical analysis as shown in the bottom of Table 3-6. It will also be instrumented with most of the same types of continuous monitors as the spiral aircraft. This aircraft will make one or two flights per day. On one day of each intensive sampling period, it will sample in the early morning (0400-0800 PDT) and in the afternoon (1400-1800 PDT). On other days it will make only a morning flight. Its flight pattern will include about four sampling orbits at constant altitude, and the flights will take 3-4 hours. In the morning, orbits will be made over Long Beach, El Monte, and at two locations offshore. In the afternoon, the offshore orbits will be replaced by inland orbits over Pomona and Riverside. One set of samples will be

Table 3-5. Toxic Air Contaminants to be Measured in the Study Region.

---

Benzene	Methyl bromide
Carbon tetrachloride	Methyl chloroform
Chloroform	Methylene chloride
Chlorobezene	Perchloroethylene
Ethylene dibromide	Trichloroethylene
Ethylene dichloride	Xylene (o-, m-, and p-)

---

Table 3-6. Aircraft Measurements

<u>Aircraft Measurements</u>	<u>Time dur/freq</u>	<u>Analytical Methods</u>
O <sub>3</sub>	Continuous over spirals and orbits. Spirals from surface to 5000'	Chemiluminescence
NO		Chemiluminescence
NO <sub>x</sub>		Chemiluminescence
SO <sub>2</sub>		Flame photometric
Light Scattering (multi-wavelength)		Integrating Nephelometer
Temperature		Thermister
Dewpoint		Cooled mirror
Turbulence		Pressure fluctuation
Position		LORAN
Altitude		Pressure sensor
Aerosol Size Distribution		OPC (PMS ASASP-X)
Hydrocarbon	In orbits and at selected spiral locations	Canisters - GC/FID
PAN	In orbits only	Impregnated filter, GC/EC
PM-2.5 mass SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> ; NH <sub>4</sub> <sup>+</sup> ; Na <sup>+</sup> SO <sub>2</sub> Carbon (elemental and organic)		Bendix 240 cyclone Gravimetric IC; AC; Atomic absorption Impregnated filter Thermal combustion
HNO <sub>3</sub>		Cyclone/denuder difference
NH <sub>3</sub>		Oxalic acid impregnated filter
Carbonyls		DNPH absorber
Tracer Samples		Mylar bag - GC/EC

obtained for about 30-40 minutes in each orbit. Typically, the samples will be obtained in the inversion layer above the surface layer (about 1000' agl) in the morning and in the middle of the mixed layer in the afternoon (about 1500'-2000' agl).

For the fall sampling, one aircraft will collect integrated samples in addition to its continuous measurements. It will perform two flights per day in the morning (0500-0900 PST) and in the afternoon (1300-1700 PST). It will focus its measurements in the western portion of the Basin, performing spirals at about five locations as well as collecting integrated samples in orbits at two locations. The occurrence of fog will restrict some flights. Occasional night flights could be made when fog is not a problem.

In addition to the in-situ airborne measurements, airborne LIDAR measurements will document the three-dimensional pollutant distribution, especially along the slopes and offshore. In conjunction with the surface and upper air winds, the LIDAR will provide useful information on the fluxes into and out of the basin at the boundaries and on pollutant ventilation and carryover processes. LIDAR flights will be made in early morning and in mid-afternoon during intensive study days. The morning flight will document layers carried over from the previous day and will map the offshore boundary conditions. The afternoon flights will document the boundary conditions and ventilation processes.

### 3.6 EMISSIONS

Our discussions with the modeling community have indicated that the quality of the available emissions data is one of the limiting factors in improving model accuracy. For three-dimensional grid models, an accurate, gridded, time- and species-resolved inventory will be necessary for each day to be modeled. For receptor models, detailed characterizations of the emissions from different sources will be needed for source identification (especially organics and trace metals).

To address the overall emissions issue, an Emissions Working Group (EWG) was formed. The group consists of university, industry, and government members and is responsible for providing the SCAQS emissions inventory. The EWG will design and execute studies to examine the accuracy of existing inventories and will coordinate special studies to improve these inventories. The EWG members are listed in Appendix A.

Emphasis will be on those species most important for oxidant and aerosol formation including organic and inorganic gases and size-resolved particulate matter. The basis for the SCAQS inventory will be the scheduled 1987 inventory update for the South Coast Air Basin to be prepared by the SCAQMD and the ARB. This inventory will be refined as necessary to include the results of special inventory characterization studies and emissions information specific to the intensive days of the SCAQS field program. The characterization studies are aimed at quantifying and reducing the uncertainties in the inventory, and thus obtaining a more accurate characterization of emissions in the Basin. The EWG will work closely with both the SCAQMD and CARB during this process.



The overall plan for compiling the SCAQS inventory is contained in a planning study (Oliver et. al., 1987) which identifies procedures and a schedule for developing the emissions data base. Two primary objectives were associated with the planning study:

- 1) To analyze available options and techniques for compiling emissions data and developing the data base; and
- 2) To develop a detailed work plan and schedule for establishing the SCAQS inventory data base.

The planning study focused greatest attention on 17 specific topics in four general areas:

- Day-specific emissions data needs.
- Procedures for estimating on-road motor vehicle use and emissions.
- Data base schedule.
- Hydrocarbon and particulate speciation.

The 17 specific topics are listed in Table 3-7.

The purpose of collecting day-specific emissions data is to focus on operating conditions and other characteristics that might lead to a significant difference in expected emissions from the average day. Much of the future air quality modeling for the Basin will center on specific days using meteorological and air quality data from SCAQS intensive periods. The EWG's objective is to construct a set of emission inventories that are as representative as possible of actual emission levels on the selected days. Therefore, using the day-specific emission-related data, the average inventory will be modified to represent the particular days in 1987 to be modeled. Since all sources cannot be "monitored" during the intensive periods, the major emission sources will receive primary emphasis under the day-specific data collection effort. In particular, the data will include traffic counts and monitoring of traffic flow, hourly power plant emissions, non-routine operating conditions at major stationary sources (including refineries and airports), a review of source data at the SCAQMD, and checks for unusual natural phenomena during intensive days (such as high winds, fog, storms, and fires).

The EWG planning study (Oliver et al., 1987) recommends a number of special studies to evaluate and reduce uncertainties in the 1987 SCAQS inventory. The details of these special studies and their priorities will be reviewed and refined by the EWG.

The EWG is working with the ARB and the SCAQMD on the details of the SCAQS inventory development schedule. The recommended schedule calls for the completion of the 1987 inventory update by the second quarter of 1990. The SCAQS inventory will then be ready for modeling applications by the third quarter of 1990. This four year overall schedule and its intermediate milestones represent a more aggressive but still realistic approach for completing the inventory than would exist in the absence of the SCAQS program.

Table 3-7. Emissions Working Group Planning Study Topics

- 
1. Data Base Schedule
  2. Emission Inventory Preparation Process
  3. Results from Model Sensitivity Runs
  4. Motor Vehicle Emission Factors
  5. Stationary Source Emissions
  6. Aerosol Characterization Data
  7. Uninventoried Sources
  8. Small Hydrocarbon Sources
  9. Area Source Gridding
  10. Vehicle Use Data
  11. Evaporative Emissions
  12. Road and Soil Dust Emission Factors
  13. Temporal Resolution
  14. HC/NO<sub>x</sub> Ratio
  15. Two Versus One Data Bases
  16. Day-Specific Data Needs
  17. Inventory Uncertainties
-

Meeting this schedule will likely require modifying some priorities in the SCAQMD and ARB inventory preparation programs.

### **3.7 METEOROLOGICAL MEASUREMENTS AND FORECASTING**

A Meteorology Working Group was formed to address the ground and upper-air meteorology measurements that are needed for SCAQS, to develop a forecasting team and protocol, and to help design the proposed tracer studies. Members of the Meteorology Working Group are listed in Appendix A. The meteorology measurements described below reflect the recommendations of the working group.

#### **3.7.1 Surface and Upper Air Measurements**

A major concern of the modeling community is that adequate characterization of the three-dimensional wind field be performed. Extensive routine surface data exist in the study area as indicated in Figure 2-1, but upper air data are quite limited. Also, the meteorology of the offshore regions should be characterized to document offshore ventilation, carryover, and re-entrainment processes. New offshore measurements are expensive, but data from existing offshore sources will be acquired and included in the data base. Additional measurements will be made on Catalina and San Nicolas Islands. Some offshore meteorology measurements will also be available from the aircraft.

The routinely-available surface and upper air meteorology data for the study period will be acquired by the data management contractor and included in the data archives. The special SCAQS meteorology measurements during the summer study include:

- one doppler acoustic sounder on intensive study days at the Long Beach A-site;
- airsondes six times per day on intensive study days at Glendora and near Anaheim;
- rawinsondes six times per intensive study day at Burbank, El Monte, Hawthorne, Long Beach, Loyola-Marymount University, Ontario, and Riverside;
- surface wind stations at elevated locations on all study days at Catalina Island, Henninger Flats, Kellogg Hill, and Palos Verdes; and
- time-lapse cameras at Mount Wilson and Palos Verdes.

The upper air measurement sites are shown in Figure 3-4. The airsonde and rawinsonde soundings will be made at 0500, 0800, 1100, 1400, 1700, and 2200 PDT in the summer. The measurement sites for the fall program have not yet been selected. The fall sounding times will be the same as the summer times in PST, i.e. the first sounding will be at 0400 PST.

### 3.7.2 Forecast and Decision Protocol

The forecasting team will issue a meteorology and air quality forecast each afternoon for the following two-day period. The forecast of PM-10 and ozone concentrations will be in terms of three categories, low, medium, and high, based on the historical distribution of ozone daily maxima and PM-10 24-hour average concentrations. The categories, with their associated cut points, are:

	High (75th percentile)	Medium (50th percentile)	Low
PM-10 (24 hr. avg.)	>105 $\mu\text{g}/\text{m}^3$	>88 $\mu\text{g}/\text{m}^3$	<88 $\mu\text{g}/\text{m}^3$
Ozone (max. hr.)	> 24 pphm	>19 pphm	<19 pphm

Days when either PM-10 or ozone are predicted to be in the high category, or when both are predicted to be in the medium category will be considered as acceptable for sampling.

The decision to start intensive sampling will be made by the Program Coordinator, based on the forecast and on the logistical readiness of the investigators and equipment. Nominally, the sampling periods will be for two days, but one- or three-day periods are possible. There will be at least a one day rest period between intensive sampling periods.

The decision to sample will be made after the afternoon forecast (about 1600 local time) for the sampling period which starts at 0000 PST the next night (about 32 hours later). If a decision to sample is made, the intensive sampling may be cancelled the next day after the forecast in the afternoon before the sampling is to start ( $\sim$  8 hours in advance).

For each intensive study day, meteorological summaries will be prepared which document cloud locations, bases, thicknesses, and durations; mixing height and inversion strength as available from temperature, wind, and acoustic sounder data; the synoptic conditions; and any unusual weather occurrences.

## 3.8 SPECIAL STUDIES

Some of the stated project objectives cannot be met with the monitoring data alone. Several special studies will be performed to address specific questions. Some of these are outlined below, but the details of their designs are not included in this plan. Most of these special studies are either self-contained data acquisition and interpretation projects or are enhancements to the existing SCAQS measurements.

### 3.8.1 Perfluorocarbon and SF<sub>6</sub> Tracer Releases

Two types of tracer tests will be performed during the SCAQS summer sampling period. One series of tests will evaluate the relative impact of elevated and ground-level emission sources on ground-level concentrations of ozone, NO<sub>2</sub> and PM-10. Four unique perfluorocarbon tracers will be used for these tests. Simultaneous releases will be made from a 200 foot stack at

a coastal generating station near Long Beach and from ground level near the stack. One pair of tracers will be released from 0400-0900 PDT during offshore flow and the other pair during onshore flow from 0900-1600 PDT. Perfluorocarbon concentrations will be measured at 50 sites throughout the Basin during the next 36 hours. Three tests will be made to examine periods with high PM-10, high ozone, and moderate ozone.

The second series of tests will involve shorter time scale releases and measurements of SF<sub>6</sub>. These SF<sub>6</sub> releases are designed to provide data to test and evaluate the dispersion and windfield components of air quality simulation models. One of these tests will involve a one hour release during conditions of light offshore flow and a low inversion. The release will be made during the early morning traffic peak in an area of high mobile source emissions in the western portion of the Basin. Hourly average measurements will be made at about 25 sampling locations for the next 12 hours. Grab samples will be taken in a series of automobile traverses to map the plume as it transports downwind.

A second SF<sub>6</sub> test is designed to determine the effect of aged ozone layers aloft on surface ozone concentrations later in the day. SF<sub>6</sub> will be released into an ozone reservoir above the surface mixed layer in the early morning. The release will probably be in the vicinity of El Monte. Sampling will take place at 25 surface sites for 12 hours or more after the release. If the first two SF<sub>6</sub> tests work out and sufficient funds are available, a third SF<sub>6</sub> release will be made into a late evening stagnant air mass in the western basin, and sampling will be conducted overnight and into the next day.

### **3.8.2 Fog Chemistry Measurements**

Fog is known to play an important role in the formation of aerosol in the SOCAB. To better understand the interactions of fog and smog, fogwater samples will be obtained during SCAQS. Active strand cloudwater collectors will be located in fogs to acquire enough sample to quantify the liquid water content, anions and cations, aldehydes, organic acids, S(IV), and hydrogen peroxide. These intermittent measurements may not correspond to SCAQS sampling days because fogs may not occur on these days. The geographical and temporal distribution of these measurements in fogwater can be used with other SCAQS measurements in support of the chemical mechanism modeling project.

### **3.8.3 Effects of Relative Humidity on Aerosol Composition and Visibility**

The liquid water content of suspended particles, as noted in Section 2, has an important influence on secondary aerosol formation mechanisms as well as on visibility reduction. A tandem differential mobility analyzer (TDMA), a nephelometer thermidograph, and a varying humidity aethalometer will be operated during the SCAQS program to determine the effects of changes in relative humidity on aerosol properties. The TDMA will determine changes in the aerosol size distributions at different relative humidities. The difference in computed particle mass for zero and ambient humidities is an approximation of the liquid water content of the aerosol. These measurements will be made at the Claremont A-site. The thermidograph will be used to quantify the influence of ammonia emissions on the hygroscopic properties of SOCAB aerosols. These measurements will be made at the Rubidoux and Claremont sites. The aethalometer will be used in conjunction with a variable dew-point

humidification chamber and size selective aerosol sampling to determine the response of carbonaceous species to changes in relative humidity. A reference which produces known quantities of liquid water will be available as a standardization and audit device for these measurements.

#### **3.8.4 Deposition Fluxes**

Large particles deposit at the ground by gravitational sedimentation, while small particles and gases deposit by turbulent transport to and absorption at the ground. A rotary impactor will be operated at the Claremont site to determine the concentrations of large particles (greater than ten microns) which are potentially present for deposition. This will be accompanied by a greased deposition plate to measure the quantity of particles which actually reach the ground. Sedimentation velocities can be calculated from these two measurements for use as parameters in particulate modeling. Deposition fluxes of small particles and acidic gases will also be determined by measurements on aerodynamic surrogate surfaces and vegetation at the Claremont site. These deposition fluxes can be combined with the ambient concentrations to infer deposition velocities for fine particles and gases.

#### **3.8.5 Acidic Species Sampler Methods Evaluation**

The ARB has conducted measurement method comparisons for nitrogenous and carbonaceous species. The acidic species comparison will be the third in this series of method evaluations. The B-site SCAQS observables include several which are also being incorporated into national and state dry deposition monitoring networks. Several non-SCAQS sampling and analysis systems will be compared during the SCAQS summer period with the collocated SCAQS measurements at Claremont. The transition flow reactor from EPRI's Operational Evaluation Network, EPA's version of the transition flow reactor, University of Denver's continuous nitric acid analyzer, ARB's dry deposition sampler, EPA's annular denuder, a turnable diode laser absorption spectrometer, a denuder difference method, and several other samplers will be operated simultaneously with the SCAQS sampler. Additional samples will be taken during non-intensive sampling periods to measure low as well as high pollution events. The data from this comparison will be used to evaluate the precision, accuracy, and validity of measurement methods used in SCAQS and in other studies.

#### **3.8.6 Visibility Measurement Comparison**

SCAQS also will provide an opportunity for a visibility measurement methods comparison. Several of the measurements cited with respect to relative humidity noted in Section 3.8.3 will provide visibility outputs and will be useful in determining the effects of different instrumental changes in humidity on visibility measurements. The B-site  $b_{abs}$  and nephelometer measurements are also available for comparison. In addition, long-path measurements of transmittance and path radiance will be made using a radiance difference technique, and contrast measurements will be made with teleradiometers. The information from this comparison will be used to address Objective 6, dealing with the validity and uncertainty of measurement methods. It will also allow the testing of visibility modules in air quality models.

### 3.8.7 Captive Air Experiments

While the testing of photochemical airshed simulation models will need all of the SCAQS measurements as a function of space and time, the testing of individual chemical mechanisms can be more easily addressed by more highly controlled experiments. Up to eight 450-liter transparent FEP-Teflon chambers will be filled in the morning and subjected to natural radiation until sundown on SCAQS intensive sampling days. Ambient air or prepared mixtures along with different initial concentrations of  $\text{NO}_x$  and ROG will be placed in the chambers, and the reaction products will be continuously monitored throughout the experiments. The experiments will be conducted at the downtown Los Angeles and the Claremont sites. The data from these experiments will be used to test different photochemical mechanisms for their potential incorporation into air quality models.

### 3.8.8 Fate of SOCAB Pollutants

The SCENES visibility study (Mueller et al., 1986) is concerned with the potential impacts from distant urban areas in the National Parks of the southwestern United States. Two studies will be conducted outside of the SOCAB to determine the chemical characteristics and the transport routes of air leaving the Basin. The Greater Los Angeles Distant Impact Study (GLADIS) will make continuous measurements of seven halocarbons, surface meteorology, and  $b_{\text{scat}}$  at Cajon Pass throughout the SCAQS period. GLADIS will also launch airsondes in the pass area. The SCENES summer intensive study will make intensive chemical measurements of halocarbons, fine particle chemistry, and particle precursors during outflow periods at Cajon Pass. A SOCAB chemical source signature of gaseous and particulate species will be measured to determine its chemical character and variability. Measurements will also be taken at distant receptors at Spirit Mountain, NV, and Hopi Point, AZ, to determine whether or not species in the SOCAB source signature can be detected. A continuous 15-station pibal network will take upper air measurements every six hours throughout the SCAQS summer period, and a primitive equations transport model will be applied to these pibal data and to SCAQS meteorological data to determine those trajectories which correspond and those which don't correspond to SOCAB contributions at the distant receptors. The SCAQS perfluorocarbon detection network described in Section 3.8.1 will be extended to these receptors to verify the model predictions of impact or non-impact from the SOCAB. This study will help complete a pollutant mass balance of atmospheric constituents in the SOCAB.

### 3.8.9 Mobile-Source Emissions Measurements

One of the most uncertain components of the emissions inventory is the mobile-source component. Field studies are planned in both a tunnel and a parking garage in order to improve the estimate of motor-vehicle emission factors. By making measurements in both tunnel and garage situations, these studies will estimate emission factors representative of tailpipe, evaporative, and wear-debris emissions under a variety of driving conditions, and with a realistic mix of vehicles. Chemical and physical measurements will be consistent with similar measurements being made during the SCAQS field studies. The vehicle emission factors estimated from this special study will be used to improve the existing estimates in emission inventories.

## 4. QUALITY ASSURANCE

### 4.1 QUALITY ASSURANCE OVERVIEW

Every measurement consists of four attributes: a value, a precision, an accuracy, and a validity (e.g. Hidy, 1985). The measurement methods described in the previous section are used to obtain the value. Quality assurance is the complementary part of the measurement process which provides the precision, accuracy, and validity estimates and guarantees that these attributes are within acceptable limits. The quality assurance component of SCAQS is essential to the attainment of Objective 1.

Quality assurance for the project will be a major responsibility of the Program Coordinator (PC). The PC must ensure that the final program design contains adequate quality control procedures and adequate external checks to assure that the data obtained will be adequate for their intended purposes. In addition, it is the responsibility of the PC to monitor the quality assurance activities during the project and to make certain that problems are rapidly identified and solved. A quality assurance program will be implemented for all repetitive measurements for which a standard operating procedure (SOP) can be developed.

The quality assurance program for SCAQS will include two types of activities: quality control (QC), and quality audits (QA). The QC activities will consist of written standard operating procedures to be followed during sample collection, sample analysis, data processing, and auditing. These procedures define schedules for periodic calibrations and performance tests. They specify pre-defined tolerances which are not to be exceeded by performance tests and the actions to be taken when they are exceeded. The QC activities are on-going activities of measurement and data processing personnel. The QC procedures will be developed, documented, and implemented by each measurement group, and reviewed for completeness by the quality auditor.

Quality auditing is an external function performed by personnel who are not involved in normal operations. The purpose of quality audits is to determine whether the QC procedures are adequate and are being followed and whether the tolerances for accuracy and precision are being achieved in practice. The quality auditing function consists of two components: systems audits and performance audits.

Systems audits will be performed for all measurements. They start with a review of the operational and QC procedures to assess whether they are adequate to assure valid data which meet the specified levels of accuracy and precision. After reviewing the procedures, the auditor examines all phases of the measurement or data processing activity to determine whether the procedures are being followed and the operational people are properly trained. The systems audit is intended to be a cooperative assessment resulting in improved data rather than a judgmental activity.

Performance audits (PA) establish whether the predetermined specifications are being achieved in practice. For measurements, the PA



involves challenging the measurement/analysis system with a known standard sample which is traceable to a primary standard. PAs will be performed for those measurements for which standards are available. For data processing, the PA consists of independently processing samples of the data and comparing the results.

For SCAQS, the position of Quality Assurance Manager (QAM) has been funded by the ARB. The QAM is responsible for the performance of systems audits and for the coordination of performance audits. Performance audits will be funded separately and may actually be performed in part by ARB, SCAQMD, or EPA staff. The QAM will report the audit findings to the PC, and QA reports will be distributed along with the data summary reports. Quality audit and quality control for the C-sites and for supplemental data will be the responsibility of the agencies operating the stations. The QAM will review and document the QA and QC procedures in use by those agencies and include such documentation with the audit reports to the PC.

For B-sites, the QAM will coordinate systems and performance audits for each appropriate measurement. In addition, standard QC procedures will be developed and implemented by the measurement groups. For A-sites, performance and systems audits will be performed for those measurement systems for which the operational procedures are standard and well documented. For more experimental measurements or those for which there is no other standard, only systems audits will be performed. It will be the responsibility of the measurement group to develop documentation and quality control procedures and to provide an assessment of the validity, accuracy, and potential sources of error in their data.

#### **4.2 ROLE OF QUALITY ASSURANCE MANAGER**

The Quality Assurance Manager (QAM) is responsible for the following tasks:

- work with investigators to determine the target specifications for accuracy and precision for each measurement;
- review the operational and QC procedures for each measurement and verify the assumptions on which the measurement is based;
- prepare systems audit procedures and submit to PC and measurement personnel for approval;
- perform preliminary systems audits at investigators' location with the help of the measurement groups;
- develop performance audit procedures for all core or routine measurements and submit to the PC and the investigators for approval. No performance audits will be done for experimental or special measurements since standards are not available;
- perform systems audits on field measurements and laboratory and data processing procedures during the field programs;

- coordinate performance audits on routine measurements during the field programs;
- for any problems identified in audits, inform the PC and review the issue with the investigator until auditor and investigator agree on the existence and extent of the problem. Try to determine a course of action for remedying the problem;
- prepare short letter audit reports for the PC and investigators within 2 or 3 days of each audit; and
- prepare detailed draft reports for the PC and investigator for each audit. Revise drafts after feedback from the PC and investigator. Submit final audit reports to the PC for inclusion in the data base.

### 4.3 DEFINITIONS

In developing a quality assurance plan, it is important that the project participants agree on the definitions of the terms used. These definitions are continually evolving (e.g. Mueller, 1980; Mueller and Hidy et al., 1983; Watson et al., 1983; Hidy, 1985), but the set to be used during SCAQS is presented below. These definitions will place all SCAQS measurement processes on a common basis.

- **Measurement:** An observation at a specific time and place which possesses four attributes: (1) value--the center of the measurement interval; (2) precision--the width of the measurement interval; (3) accuracy--the difference between measured and reference values; and (4) validity--the compliance with assumptions made in the measurement method.
- **Measurement Method:** The combination of equipment, reagents, and procedures which provide the value of a measurement.
- **Quality Assurance:** A combination of procedures, reference materials, and controlled tests which assure the precision, accuracy, and validity of the measurement and minimize the exceedance of pre-set tolerances for these attributes.
- **Quality Control:** Internal procedures, documentation, and performance tests which: (1) identify deviations from measurement assumptions and (2) identify measurement values which exceed pre-set tolerances when compared to internal reference materials. Quality control identifies and corrects measurement method deficiencies and provides the information needed to assign the precision and validity attributes to the measurement.
- **Quality Audit:** External procedures, documentation and performance tests which: (1) determine the adequacy of internal procedures, documentation and performance testing, (2) ascertain the degree to which internal quality control is following the prescribed procedures, and (3) challenge the measurement methods and internal reference materials with known values derived from an external reference material. Quality auditing identifies quality

control deficiencies and provides the information needed to assign accuracy attributes to the measurement.

- Primary Standard: A known quantity of a material which is derived from fundamental physical principles, is reproducibly quantified by many different measurement methods, maintains its integrity over time, is subject to periodic and documented verification, and is accepted by all measurement methods as a standard.
- Primary Reference Material: A known quantity of a material which is reproducible within individual measurement methods, but not among methods. A primary reference material is accepted by all measurement methods as being precise, but not necessarily as being accurate.
- Transfer Standard: A physically similar quantity of material which can be directly traced to an identified primary standard or primary reference material via periodic documentation of comparisons using a prescribed measurement method. Transfer standards are used for calibration, quality control performance tests, and performance audits.
- Traceability Trail: The documentation which establishes the relationship between any measurement and all of the primary standards or primary reference materials.
- Measurement Method Validity: The identification of measurement method assumptions, the quantification of effects of deviations from those assumptions, the ascertainment that deviations are within reasonable tolerances for a specific application, and the creation of procedures to quantify and minimize those deviations during a specific application.
- Sample Validity: Procedures which identify deviations from measurement assumptions and flag individual measurements as valid, valid but suspect, or invalid based on pre-defined criteria.
- Developmental Status: Indicates the degree to which a measurement method can be expected to yield values of known precision, accuracy, and validity. Measurement developmental status can be "established", "semi-established", or "unestablished." Established methods are those with accepted operating procedures, identified and quantified interferences, traceability to accepted primary standards, agreement with other established methods, and known levels of precision, accuracy, and validity. Semi-established methods are those with controversial operating procedures, partial characterization and quantification of interferences, traceability to one or more reference materials, disagreement with other established or semi-established methods, and known precision levels. Unestablished methods are those with incomplete or non-existent operating procedures, no traceability to primary reference materials

or standards, little or no inter-method comparison results, and unknown precision, accuracy and validity.

- Measurement Process: Established or semi-established measurement methods combined with quality control and quality auditing to provide values with known precision, accuracy, and validity.

#### 4.4 STANDARD OPERATING PROCEDURES

Standard Operating Procedures (SOPs) codify the actions which are taken to implement a measurement process over a specified time period. These are both descriptive and prescriptive. The various SOP revisions are maintained so that subsequent users of the measurements may consult them to interpret measurements in light of new knowledge about the measurement methods being applied. Examples of this descriptive use were given in Section 2.2. The prescriptive role of SOPs is to incorporate state-of-the-art knowledge into current measurement practice. SOPs must undergo scheduled revisions in order to fulfill this prescriptive mandate.

Standard operating procedures will be created for routine field sampling, laboratory analysis, data processing, and quality audit activities planned for SCAQS. These procedures should include the following elements:

- A brief summary of the measurement method, its principles of operation, its expected accuracy and precision, and the assumptions which must be met for it to be valid.
- A list of materials, equipment, reagents and suppliers. Specifications should be given for each expendable item, and its storage location should be listed.
- Designation of an individual to be responsible for each part of the procedure.
- A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification.
- Startup, routine, and shutdown operating procedures and an abbreviated checklist.
- Copies of all data forms with examples of filled out forms.
- Routine maintenance schedules, maintenance procedures, and troubleshooting tips.
- Internal calibration and performance testing procedures and schedules.
- External performance auditing schedules.

- References to relevant literature and related standard operating procedures. The Program Coordinator is responsible for acquiring standard operating procedures from all measurement investigators and for scheduling procedure revisions. The Quality Assurance Manager is responsible for reviewing procedures and determining their completeness and accuracy.

#### 4.5 SAMPLE VALIDATION

The results of several measurement method validation studies have been reported in Sections 2 and 3. Section 6 specifies several projects for the interpretation of the results of these studies. These results will be needed to provide a basis for the validation of individual samples taken within SCAQS. Three levels of validation will be applied with the result being a label of valid, valid but suspect, or invalid associated with every measurement.

Level I sample validation takes place in the field or in the laboratory and consists of: (1) flagging samples when significant deviations from measurement assumptions have occurred, (2) verifying computer file entries against data sheets, (3) eliminating values for measurements which are known to be invalid because of instrument malfunctions, (4) replacing data from a backup data acquisition system in the event of failure of the primary system, and (5) adjusting of measurement values for quantifiable calibration or interference biases. Each measurement investigator performs Level I validation on his measurements.

Level II sample validation takes place after data from various measurement methods have been assembled in the master data base. Level II applies consistency tests based on known physical relationships between variables in the assembled data. Examples of these tests are: (1) the sum of all chemical species in a particulate matter sample should be less than or equal to the gravimetric mass of that sample, (2) size segregated particle concentrations should be less than total particle concentrations, and (3) dew point should always be less than temperature. Data adjustments for quantifiable biases are made in Level II validation if they are discovered after assembly of the master data base. The Data Manager, cooperating with the measurement investigators, is responsible for Level II validation.

Level III sample validation is really a part of the data interpretation process. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are usually identified during the data interpretation process as: (1) extreme values, (2) values which would otherwise normally track the values of other variables in a time series, (3) values for observables which would otherwise normally follow a qualitatively predictable spatial or temporal pattern. The Program Coordinator, with cooperation from the Data Manager and data interpretation investigators, is responsible for Level III validation.

All data validation actions at each level should be recorded in a data validation summary which accompanies the data volumes. Data base records

should contain flags to identify the level of validation which they have received at any point in their existence.

## 5. DATA MANAGEMENT

### 5.1 ROLE OF DATA MANAGER

The Data Manager (DM) will be responsible for assembling, archiving, reviewing, and distributing the data obtained during the study. Specifically, the DM will perform the following tasks:

- With the concurrence of project participants, develop a data exchange protocol. All participants must agree to abide by the protocol in order to use study facilities and to obtain data from the data archives before publication of the final report.
- With the help of the participants, identify all data to be considered part of the study. (Some participants or other groups may obtain data for their own use which are unrelated to the study.)
- Develop standardized data formats with the assistance and approval of the participants. All participants will submit their data to the DM in the agreed upon format and media after each study period.
- Review all data submitted to determine that formats are proper and documentation is adequate.
- Identify sources, formats, and quality of data available from existing data resources (National Weather Service, Federal Aviation Administration, AQMD, etc.) and prepare a list of data to be obtained for the study.
- For each sampling day, obtain routinely available data, convert to project format, and archive.
- For each intensive study day, obtain all project data.
- Archive all data in an easily reproducible and retrievable form. The data should be archived using a disk-based data base management system so that data required for specific analyses can be easily accessed.
- Perform simple consistency and validity checks (Level II) on the data submitted, and flag those data points which are suspect. When possible, review suspect data with the responsible group and resolve the status of the data.
- Correct or flag data points in the master data base when errors are identified by subsequent users of the data.
- Prepare a report which inventories the data base for each study period and which documents the data formats and data access procedures. Summaries of data capture rates and data validity should be included for each intensive study period. Provide report to all participating and sponsoring organizations.

- Provide data to participants on request as required for their analyses.
- Provide a copy of the complete data archive to ARB.

The DM will design formats for the data to be submitted that are useful for the modeling community. Except for the data from the existing data resources, the DM should not have to reformat the data obtained from the participating organizations.

## 5.2 DATA BASE DESCRIPTION

The data base will have two components. A core data base will be developed for modeling and data analysis use. The core data will consist of the emissions data, the available routine supplementary data, the data from the B- and C-sites, the aircraft data, the surface and upper air meteorology data, and data from the A-sites which are from regularly repeated measurements over extended time periods and which are of known accuracy and validity. The second component of the data base will be the special studies measurements such as the tracer studies and measurements from the A-sites which are more experimental in nature.

All data should be submitted in consistent and easily usable formats with like types of data being formatted similarly. Data formats should allow easy use of the data with graphics, statistical and modeling software. All data should be reviewed and validated (Level I) by the group submitting the data, and suspect data points should be flagged in the data records.

All data submitted to and assembled by the DM should be accompanied by reports which describe the data formats, uncertainties, detection limits, and accuracy estimates for the data. Much of this information should also be included in the data records. A hard copy printout should accompany all data. These data reports should also provide an inventory of the data submitted and a summary of the data validity and data capture rates for each intensive study period, and describe the data collection, quality control and validation procedures used to obtain and process the data. The report should discuss potential errors, interferences, or other caveats regarding the data.

The formats of the core data should be such that they can be included in a single large data base and are easily accessible by modelers. Data records should include space for validity flags and other similar notation. Formats of the special studies data will, by necessity, be more varied and less standardized. Whenever possible, however, data records should document the position, time, and sample averaging period.

Core data will be reviewed by the DM and subjected to simple consistency or validity checks. Flags for suspect data points will be added to the data records by the DM.

Core data should be submitted to the DM within six months of the end of each field study and special studies data as soon as possible after that. Data should be available to participants within about 3 months after receipt by the DM.



### **5.3 ACQUISITION OF SUPPLEMENTAL DATA**

The DM with the assistance of ARB staff will be responsible for identifying and acquiring existing supplemental data. These data include NWS, FAA, and other available meteorological data and air quality data from SCAQMD, ARB, Ventura County Air Pollution Control District and other available sources. Such data obtained by the DM will be reformatted to be consistent with the core database formats for similar types of data. Potential sources of supplemental data are identified in Section 2.

### **5.4 DATA EXCHANGE PROTOCOL**

A data exchange protocol has been prepared with input from the sponsors. The purpose of the protocol is to ensure timely and complete availability of the data collected as part of SCAQS and proper attribution for data used in analyses and publications. It will be a condition of participation in the program that sponsors and participants agree to abide by the protocol.

The approved protocol is shown in Figure 5-1.

## Southern California Air Quality Study

### Data Exchange Protocol

The following is the SCAQS Data Exchange Protocol. The purpose of this protocol is to ensure timely and complete availability of the data collected as part of SCAQS and proper attribution of data used in analyses and publications.

1. The data collected are to be available eventually to the scientific community. Before final publication, however, the data will be made available to the SCAQS participants. It is expected that each participant will submit at least the type B data from each field study to the Data Manager within 6 months of the end of each field study. Type A studies data may take a few months longer. Data should be submitted in the SCAQS-specified format and should be reviewed and validated by the participant prior to submission. Participants will keep the sampling and processing documentation for their own data for 5 years after the field study.
2. All data in the SCAQS data bank will be available to any participant on request. No participant should publish analyses or data sets which include data of other participants unless he/she has the permission of the other participants who provided the data or the data have been formally released to the public. Participants may distribute or publish their own data at any time subject to the conditions in 4, below.
3. The sources of data should be cited whenever data are used in publications. If a substantial amount of data from other participants is used, that participant should be given the option of being included as a co-author on resulting publications.
4. Prior to submission for publication or presentation, manuscripts resulting from SCAQS should be submitted to the participants and all SCAQS sponsors for comment. Each participant and sponsor will have 30 days from receipt of the manuscript to submit his comments to the senior author. The authors should give sincere consideration to all comments. If the comments are not incorporated in the manuscript, the commenting participant may submit his comments separately to the journal to which the original manuscript will be submitted.

We agree to abide by the principles of the SCAQS Data Exchange Protocol -

----- NAME	----- TITLE
----- ORGANIZATION	----- DATE

## **6. DATA ANALYSIS AND INTERPRETATION**

### **6.1 ROLE OF DATA ANALYSIS COORDINATOR**

In a study of this type with many investigators and many types of data analysis and interpretation, it is necessary to have one person who can keep track of the project objectives and coordinate the diverse analysis efforts so that the objectives are met. The Data Analysis Coordinator will have the following tasks.

- Identify data analysis methods to meet each of the final project objectives.
- Identify the participant who will perform each analysis task.
- Identify the information and data needs for each analysis task.
- Work with the various investigators to develop a critical path diagram and identify when the investigator will need which information or data.
- Identify milestones for review.
- Act as a facilitator to assure that the required data are made available to the investigators on schedule and that investigators are aware of complementary efforts by other investigators.
- Identify duplications of effort and work out agreements between investigators to minimize unproductive efforts and maximize the technical output from the resources available.
- Identify topics for presentation at a technical session and coordinate with the investigators to assure that papers are presented on all appropriate topics.
- Synthesize and integrate individual data interpretation efforts into a coherent whole.
- Assemble and edit technical papers in a published document.

### **6.2 DATA INTERPRETATION METHODS**

Measurements, by themselves, say nothing about the causes of air pollution and the likely effects of emissions reductions. It is only when these measurements are interpreted that relationships can be observed and conclusions can be drawn. The data interpretation methods which address the objectives stated in Section 1 need to be defined, at least in a general manner, before the first measurement is taken in order to assure: (1) that all information needed by the method will be available at the interpretative stage, and (2) that scarce resources will not be expended on taking measurements which do not fit within the data interpretation framework.

Section 1 stated the issues which might be resolved by SCAQS. Section 2 specified the additional data needs which model developers and users feel are

currently lacking. Section 3 listed the feasible measurements which would fulfill those needs. The goal of this section is to identify the data interpretation methods which are expected to be used and to associate the proposed measurements with their use in these methods.

As a result of the literature survey in Section 2, it was found that data interpretation methods appropriate for attaining SCAQS objectives generally fall into one of five categories:

- Descriptive methods summarize the spatial, temporal and statistical distributions of individual observables. They include averages, standard deviations, maxima, minima, spatial isopleths and time series. A large number of measurements of each observable (typically greater than 50 to 100) is necessary to determine statistical distributions. The period between measurements needs to be smaller than that over which major changes occur, and the geographical spacing between measurements needs to be less than the spatial frequency of the observables. The results of these descriptive methods show which observables are reaching levels of concern. Descriptive methods do not yield cause and effect relationships nor do they anticipate how a change in one variable will affect the values of other variables. These descriptive methods are often useful for the display and comparison of results from other data interpretation methods.
- Co-variation methods calculate measures of association between two or more variables. These measures take on high absolute values when the variables change in the same manner over a period of time or over a geographical area; they take on low absolute values when this co-variability is lacking. Time series analysis, correlation coefficients, and principal components analysis are methods which provide these measures of association. By themselves, these co-variation methods only establish whether or not the values of a set of variables change in the same way. When these co-variational methods are combined with a physical understanding of the situation under study, cause and effect relationships among the variables may be inferred.
- Classification methods select specific periods of time, usually periods of high pollutant concentrations, and describe the physical cause and effect relationships using all data which can be acquired. Both qualitative and algorithmic classifications are possible. Regime analysis (Keith and Selik, 1977), discriminant analysis (Lin, 1982), and case studies (Blumenthal et al., 1978) have all been applied to data in the South Coast Air Basin. The case studies are particularly useful in determining the relative importance of different chemical and physical pathways. Cases can be separated into dichotomous groups in which a pathway is expected to dominate or in which it is expected to have a negligible effect. If the expected consequence is observed in the first group and not observed in the second group, then the pathway can be considered important. Most of the quantitative physical and chemical mechanisms present in current models have resulted from their identification in case studies. The importance of various reactive species, atmospheric moisture, and liquid water content of the aerosol remain to be examined by this method.

- Source oriented models contain mathematical descriptions of the interactions among variables. These models include transport and chemical mechanisms. Lloyd et al. (1979), Reynolds et al. (1976), Cass (1979), McRae et al. (1982a), and Seigneur et al. (1983b) have produced and tested such models appropriate for the SOCAB. Each of these source models requires three-dimensional wind fields (speed, direction, and dispersion characteristics at all points in the modeled area) over a period of one day or more. These wind fields can be interpolated from measurements (e.g. Goodin et al., 1980) or calculated from fundamental physical equations applied to a set of initial conditions (e.g. Pielke, 1984). Although the transport and chemical components are usually combined in the computer implementation of each model, it is possible to introduce alternative wind fields to simulate the transport mechanisms and alternative photochemical and aerosol mechanisms to simulate chemical interactions.
- Receptor models use chemical and physical measurements of sources and receptors. They require input data for the chemical compositions of the emitting sources and ambient concentrations of those same chemical species. Linear regression of species on principal components has been shown to relate sulfate concentrations to physical causes (Henry and Hidy, 1979). Chemical mass balance calculations (Gartrell and Friedlander, 1975; Miller et al., 1972; Cass and McRae, 1983; Feigley and Jeffries, 1979) can be applied in the SOCAB to determine the contributions of source emissions to receptors. Linear regressions of  $b_{scat}$  on selected chemical species or on source contributions can be applied to determine visibility extinction budgets (White and Roberts, 1977; Pratsinis et al., 1984).

Each of these data interpretation approaches has been designed around available data, with certain assumptions being made to compensate for the missing data. Most computer implementations of these models are quite flexible owing to their intended applications in many areas with varying data availability. There is no absolute list of data needs for any of these data interpretation methods. Presumably, the more data they have the better. In several cases (e.g. Seigneur et al., 1981a, 1981b), the effects of more or less data on the results of the data interpretation method have been evaluated. There is as yet, however, no objective means of defining the optimum set of data required by a data interpretation method, nor is it possible to generally determine when additional measurements would be redundant (unless those measurements are already available).

### 6.3 DATA USES

Data can be used for four purposes in the data interpretation process:

- Input data. Every interpretation method requires some data on which to operate for the period of time being examined. Descriptive methods require values of the variables of interest in space and time. Source models require boundary and initial conditions of precursor, intermediate, and end-product species as well as three-dimensional wind fields and atmospheric stability estimates. Receptor models require ambient concentrations and source composition. When these variables are measured for the time being simulated, they are considered input data.

- ⑥ Parameters. Parameters are constants supplied to the data interpretation process by a theoretical calculation, by measurements made elsewhere and assumed to be appropriate for the place and time being studied, or by tacit assumption that the value of a variable is negligible. Reaction rates, emission rates, transformation rates, dispersion parameters, and source compositions are common parameters in source and receptor models. Values for these variables are rarely measured over the period of time being modeled. Parameters normally carry higher levels of uncertainty than input data because they are not specific to each case being studied.
- ⑥ Testing data. Values yielded by the data interpretation method can be compared with measurements of the same observable to test the extent to which the interpretation represents reality. The most common test measurements are ambient concentrations of an observable which are compared with the prediction of a source model. These two values are often uncorrelated, and they often tell little about the reasons for differences between predictions and measurements. Measurements of intermediate species over the appropriate time-scales are better tests of the data interpretation method. More complete (in space and time) measurements of model input variables can also be classified as test data when they would not be available during a routine application. The difference between model calculations with and without these input data provides an estimate of the accuracy to be attached to the model results. The final use of test data is to verify that the data interpretation method is valid for a specific application. Test data can be used to quantify deviations from model assumptions. In many cases, these deviations from assumptions can be directly related to deviations of model predictions from their true values. Parameters and neglected effects are amenable to this quantitative testing of model principles and assumptions.
- ⑥ Uncertainty estimation. The numerical values determined by any data interpretation process differ from reality because of both model uncertainty and measurement uncertainty. Model uncertainty results from deviations from the principles and assumptions of the model during its application. This model uncertainty is quantified using data in its testing role, as described earlier. The measurement uncertainty of a model calculation results from the fact that each input datum and parameter does not define a single value, but an interval within which the true value of the observable should fall. The combination of all of these measurement intervals should yield an interval around the model calculation. Very few air quality models in use today provide for the estimation of this interval, and methods to calculate it are still in their developmental stages (e.g, Efron 1979; McRae et al. 1982b; Freeman et al. 1986; Watson et al. 1984). Each one of these methods requires some estimate of the statistical distribution and width of the intervals associated with the input data and parameters. This interval is typically more than the uncertainty associated with an individual measurement. Most models assume that a single point measurement represents a volume or a period of time, and an estimate of the variability of the input data or parameter over that volume or time period is required to calculate the measurement uncertainty associated with a model calculation. Measurements which are "collocated" with a resolution finer than the temporal and

spatial scales of the data interpretation methods can be used to estimate the uncertainty of input data and parameters. These uncertainties can also be estimated from periodic performance tests of each measurement method (Watson et al. 1983). It is presumed that future model development will include methods to take advantage of this information and supply intervals associated with measurement uncertainty on model results.

## **6.4 SCAQS DATA INTERPRETATION PROJECTS**

The measurements proposed in Section 3 can be used in an infinite number of combinations as input, to estimate parameters, to test the principles and assumptions of the data interpretation methods, and to estimate the uncertainty of the quantitative results of the interpretive efforts.

Data interpretation projects are described in this section which address the objectives and issues in Section 1. The projects which follow cannot identify every way in which the SCAQS data can be interpreted. The project descriptions are presented as examples to demonstrate that each piece of data collected does have a use for input, parameterization, testing, or uncertainty estimation. Although these projects are organized by the specific objectives and issues which they are intended to address, most of them are applicable to more than one objective.

Although Sections 2, 3, and 6 appear as separate entities in the program plan, they were actually formulated in an iterative fashion. Previous research in the SOCAB was studied to determine which data interpretation methods had been used in the past and the measurements they required. These were used to define an initial set of variables to be measured in SCAQS. These measurements were then incorporated into an interpretive framework which ultimately resulted in the projects described below. The measurement set was then modified to accommodate the anticipated data interpretation needs. This iterative process is not perfect, and it may still be found that the SCAQS measurements are not totally adequate for all purposes which might be identified a posteriori. It is expected that the number of these cases will be minimized, but not eliminated, by this iterative process.

### **6.4.1 Objective 1: Description of SOCAB Air Quality**

The data base will contain individual numbers which have been validated, corrected, and flagged. In order to be of use to researchers, this data base needs to be described statistically, graphically and phenomenologically. While most researchers will do this to a certain extent by themselves, a number of summaries have been produced in past studies which have been useful in focusing the more detailed analysis of specific situations. The data description projects are intended to provide this common denominator for subsequent projects. It is recognized that no "descriptive" study can be separated from the posing and testing of hypotheses based on previous work, and it is expected that the researchers performing projects intended to address the first objective will implicitly address other objectives as well. No attempt is made to exclude this possibility in the descriptions of the SOCAB air quality data. This speculation on cause and effect relationships is considered a "bonus" of an otherwise mundane presentation of results.

### Project 1.1: Data Description Summaries of Ground-based Measurements.

Prepare statistical summaries consisting minimally of maximum, minimum, average, standard deviation, and median values for each observable at each site for the duration of both sampling periods. Express these in tabular formats and as box plots. Composite and statistically summarize one hour samples for comparison with samples of longer duration. Calculate correlation coefficients among each of the variables over space and time. Prepare graphical displays which include spatial isopleths of each observable for each four-hour period, time series plots of each observable, and surface wind flow patterns for each period. Produce graphs of concentrations obtained on all aircraft traverses with the flight paths clearly indicated on a map of the Basin and appropriate time-markers denoted on those paths. Plot average vertical distributions from all the spirals at each location for each measured observable. Plot temperature and wind sounding data for every sounding site and time plot. Plot gridded emission rates for each pollutant for the aggregate totals, elevated and ground level sources, and mobile and stationary sources over four hour intervals. Prepare a map of all major single point and area sources coded for source type. Prepare isopleths of the spatial distribution of the most reactive hydrocarbon emissions. To determine how random measurement errors change the data summaries, create ten or more simulated SCAQS data sets by adding and subtracting random numbers proportional to the uncertainties of each measurement and generate selected statistical and graphical summaries for comparison. Distribute these randomized outputs with the real outputs so that subsequent studies can use them to evaluate the differences in data interpretation results which might result from measurement uncertainty.

The output of this analysis project is expected to be used in subsequent analyses. In general, each investigator will produce those graphical and statistical displays which are of greatest use to him. The displays described here are the lowest common denominator for subsequent interpretive efforts, yet they will result in reams of paper.

An alternative to the generation, compilation, and distribution of hardcopies of these statistical and graphical summaries is the creation of a micro-computer based hardware/software system and appropriate documentation which would allow each investigator to classify the data base in any way he chooses, including the definition of new variables from the raw data, and to display it by any of the graphical or statistical techniques which have been designated above. Communications packages are commercially available which would allow most investigators to transfer data from their microcomputers to their larger computers for more intensive computations, should they be necessary. ARB is currently sponsoring a project which will interface its routine meteorological, emissions, and air quality data bases to IBM-XT disks. Reformatting routines and appropriate user instructions are being developed to interface these data with commercially available computer programs which perform data base management (Ashton-Tate, 1984), air quality data summaries (Odessa Engineering, 1985), spreadsheet and graphics (Lotus Development Corporation, 1983), comprehensive statistical analyses (Dixon et al., 1983), Chemical Mass Balance modeling, and elementary UNAMAP dispersion modeling (Bowman, 1985).

Another alternative to hardcopy printout is being explored by Pitchford and McGown (personal communication, 1985) in the RESOLVE program. The spatial



and temporal distributions of variables have been generated on a microcomputer and recorded on video tape or a video disk. Hussey et al. (1983) applied this method to air pollution data from the SOCAB with striking results. Henry (personal communication with Ron Henry, USC, 1985) is investigating its use in visibility studies. The adaptation of such a graphics display to microcomputers and interfaces to the commercial software packages described earlier would facilitate data interpretation in the SCAQS and leave a lasting legacy for subsequent air quality measurement programs.

Project 1.2: Meteorological and Upper Air Descriptions. Describe in detail each of the episodes obtained from the SCAQS in the style of Smith et al. (1972, 1984) and Blumenthal et al. (1978). These descriptions of the meteorological evolution will provide a qualitative understanding of the transport situation, convergence zones, the potential for mixing from aloft, and carryover from previous days. This qualitative description can be used to test the assumptions of the quantitative mathematical models describing transport in the basin. Surface trajectories can be inferred from the surface wind plots. Draw cross-sections of observable values obtained from aircraft vertical soundings and estimate mixing heights. Plot isopleths of mixing height for each aircraft sampling period. Examine the synoptic weather maps and correlate with the surface and upper air observations. Examine the differences between daytime and nighttime spatial distributions and determine outflow and ventilation scenarios. Compare the SCAQS descriptions with those of earlier studies such as Blumenthal et al. (1978), Smith et al. (1972), Angell et al. (1976), and Edinger (1959, 1973).

Project 1.3: Aerosol Data Descriptions. This project consists of the examination of the chemical, spatial, temporal, and size distributions of ambient aerosols, the comparisons of ostensibly equivalent methods of aerosol measurement, and the comparison of the SCAQS aerosol distributions with those derived in previous studies of Whitby et al. (1972), Hidy and Friedlander (1972), Heisler et al. (1973, 1980), Hering and Friedlander (1982), and Stelson and Seinfeld (1981). Calculate the material balance of the fine and coarse mass for each sample by converting elemental, ionic, and carbon measurements to probable compounds, summing, and ratioing to the gravimetrically measured mass concentration. Display these ratios as a time series and identify those which differ substantially from unity. Sum the four-hour total masses and ratio to the TSP mass concentrations for simultaneous samples. Produce pie charts which show the relative contributions of different chemical species to each fine and total mass concentration. Locate these pie charts on maps of the Basin with radii proportional to the total mass concentration at a site, similar to the display in Shah (1981). Identify the predominant size range of measured chemical species and compare with earlier findings. Plot four hour average number, surface area, and volume distributions as a function of particle size as derived from electrical mobility and optical particle counter data. Identify commonly recurring size distributions. Classify each sample according to one of the size distribution patterns. Plot the mass median diameters and standard deviations for each mode of the volume distributions on maps for each sampling period. Describe the evolution of the size distributions by location and time of day and compare to hypotheses advanced in previous studies such as Whitby et al. (1972), Hidy and Friedlander (1972), Heisler et al. (1973), and Heisler and Friedlander (1977). Examine similar size distributions and temporal/spatial plots using the

chemically specific size distributions obtained from the multi-orifice impactors.

Project 1.4: Nitrogen, Sulfur, Carbon, and Oxidant Budgets. Plot pie charts of the gaseous and particulate nitrogen ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ , PAN,  $\text{NH}_3$ ,  $\text{HONO}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3$ ), sulfur ( $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , organic sulfur), carbon-containing (elemental and organic particles, hydrocarbons, organic sulfur), and oxidizing ( $\text{O}_3$ , OH,  $\text{H}_2\text{O}_2$ , PAN,  $\text{NO}_3$ ,  $\text{HO}_2$ ,  $\text{RO}_2$ ) species for each four hour period on a map of the Basin. The radius of each pie should be proportional to the total number of N, S, or C atoms in the budget. Also plot these totals as time series stacked bar charts for each station, with the bars divided in proportion to the species present. Compare the more completely speciated budgets at the A-sites with the less speciated budgets at the B-sites to estimate the potential magnitudes of the missing components at the more spatially representative sampling sites.

#### **6.4.2 Objective 2: Source Characteristics for Receptor Models**

Project 2.1: Identify Chemical and Physical Properties of Sources. Compile comprehensive primary emissions profiles for source types in the SOCAB from SCAQS source characterization tests and previous studies such as Taback et al. (1979), Mayrsohn et al. (1977), and Oliver and Peoples (1985). Classify these by source type (e.g. motor vehicle, fuel oil combustion, solvent use, natural sources, etc.), and construct comprehensive emission profiles which include gaseous as well as particulate chemical composition. Based on previous studies of chemical interactions, classify each of these species as transforming or non-transforming at distances close to and distant from an emissions source. Perform principal components analysis (e.g. Hopke, 1982 with the suggestions of Henry, 1985) on gaseous and particulate data sets at A-sites and determine whether or not the expected source composition patterns are reproduced. Examine the chemical species associated with each principal component and determine whether or not source categories other than those identified from the emission inventory are affecting the receptors. Create spatial plots of selected chemical species emissions patterns and superimpose trajectories obtained from Project 1.1 to determine sampling sites and times which are most likely to be influenced by source emissions. Apply the Chemical Mass Balance receptor model using the effective variance weighting and error propagation scheme (Watson et al., 1984) to the receptor data using the profiles and chemical species for sources which are most likely to affect the receptor and which will experience minimal fractionation between source and receptor. Apply the CMB to situations when meteorological and emissions conditions mitigate against a source affecting a receptor, evaluate the consistency of the calculated source contributions with this low-impact situation. Determine the variability of CMB calculations as a function of alternative, but equally valid, source profiles, the chemical species measured at the receptor and at the source, the grouping of individual sources into source types, and in response to randomized input data. Apply the singular value decomposition method of Henry (1982) to determine the collinearity of source profiles in different situations. Determine the minimal number of chemical species and the variability which can be tolerated in their measurement for the accurate apportionment of particulate matter, carbon monoxide,  $\text{SO}_2$ , and hydrocarbon receptor concentrations in the absence of source profile fractionation.

Project 2.2: Source Profile Fractionation. Using simple equilibrium, reaction, decay, and deposition considerations (e.g. Stafford and Liljestrand, 1984), calculate the expected changes in source profiles as a function of meteorological variables and the presence of other species. Coordinate with source-modeling projects to obtain a better description of source profile evolution from the more comprehensive chemical transformation mechanisms included in these models, and compare the simple transformation estimates with these more complex ones. Calculate transport times below which no significant fractionation will have taken place and beyond which equilibrium will have been reached. Select those species for which fractionation estimates are reasonably robust. Select cases, using the results of Projects 1.1, 1.2, and 1.3, in which the constituents measured at one of the source-area sites follow a trajectory passing over several monitoring stations, and calculate the expected changes in the combination of source profile for the selected chemical species. Apply the CMB at each site along the trajectory. Linear combinations of fresh and aged source profiles, weighted by emission rates from the emissions inventory, should be constructed and applied to determine their value in the transport region for which equilibrium has not been reached. Determine the variability of the calculated source contributions to PM-10, NO<sub>2</sub>, CO, hydrocarbons, and toxic substance concentrations as a function of the variables included in the CMB. Randomize the input data in proportion to their uncertainties and estimate the uncertainty which can be tolerated. Determine the collinearity of source profiles for various source contribution levels. Compare the effectiveness of source attribution by this method for highly reactive and non-reactive sampling periods.

Project 2.3: Attribution of PM-10 to Primary/Secondary and Natural/Anthropogenic Sources. Using the results of projects 2.1 and 2.2, construct source profiles for primary and secondary categories. Primary source profiles may consist of a number of individual source type profiles. Secondary source profiles may consist of those produced by several different conversion pathways. Similarly, construct source profiles for natural and anthropogenic source types. Apply the chemical mass balance receptor models to aerosol and gas data collected at urban and non-urban sampling sites for both the fall and summer periods and for the year-long 24-hour sampling periods. Calculate the contributions of each source type to the twenty-four hour and annual average concentrations of PM-10. Examine CMB diagnostics to determine the validity of each application. To determine the uncertainty of source attribution, compare the results derived from: (1) different combinations of sources and chemical species applied to the same receptor data, (2) randomized values for the receptor and source measurements, and (3) source apportionments derived from source models applied to the same samples.

#### **6.4.3 Objective 3: Dependence of Particle and O<sub>3</sub> Formation on Meteorological and Precursor Variables**

Project 3.1: Principal Components Analysis. Develop a list of phenomena which can be represented by each SCAQS variable. These phenomena may be different for the same observable measured at a different place or time in the SCAQS network (e.g. NO<sub>2</sub> measured at night or during the day, at ground level or above the inversion, etc.). Submit these variables, excluding particulate matter and O<sub>3</sub> concentrations, to principal components analysis (e.g. Henry and Hidy, 1979). Apply the PCA to various subsets of variables to (1) obtain a stable solution and (2) determine the variability within a stable solution

after the fashion of Watson et al. (1985). Randomize the PCA input data in proportion to their measurement uncertainties and estimate the effects on the certainty of model results. Apply various factor rotation methods to determine the variability caused by the selection of a rotation. Associate each mathematical factor with a physical phenomenon on the basis of the variables on which it is loaded. Calculate the linear regression coefficients of fine and coarse particulate matter and ozone on the factor scores of each factor. Generate scatterplots of the values predicted by these regression equations and observations to determine how well the factors explain the observations. Recalculate these regression coefficients with a reduced data set and compare them to the coefficients obtained from the entire data set. Use the coefficients from the reduced data set to estimate particulate and ozone values which were excluded and compare the predicted and observed values. Examine the products of regression coefficients and factor scores and select very high or low values. Examine the results of projects 1.1, 1.2, and 1.3 to ascertain whether or not the principal components analysis is consistent with the qualitative meteorological and air quality features for the high and low products.

Project 3.2: Case Studies of the Aerosol Dependence on Liquid Water. Examine the temporal and spatial evolution of particle sizes and compositions yielded in Task 1.2 and explain them in terms of the variation of other atmospheric variables depicted by Task 1.1. Divide SCAQS data into periods which were preceded by or contain high and low RH, fogs and no fogs, rain and no rain. Examine the chemically speciated size distributions for these periods and determine whether or not there is a change in size or shape for ionic species. Calculate average size distributions and standard deviations for each of these dichotomous categories and determine whether or not they differ significantly to test the hypotheses of Hering and Friedlander (1982). Examine liquid water measurements to determine how the liquid water content of the particles varies according to the ionic composition, relative humidity, and the presence of other species, and compare this to calculations using theoretical formulations (e.g. Russell et al., 1983; Stelson and Seinfeld, 1982; Bassett and Seinfeld, 1983). Calculate ion balances for cases in which liquid water is present and when it is not and infer missing species. Determine those conditions under which liquid water content can be inferred from the ionic composition measured on a filter sample which has gone through normal filter processing procedures. Identify the potential for metal catalysts which might promote liquid-phase reactions. Stratify data by cases in which photochemical and liquid phase reactions should be dominant and estimate transformation rates for  $\text{SO}_2$  and  $\text{NO}_x$  along trajectories, then compare the results.

Project 3.3: Case Studies of Ozone Formation. Stratify episodes by high and low photochemical potential days, and compare photochemical products along trajectories identified in Project 1.1. Further stratify these episodes by  $\text{ROG}/\text{NO}_x$  ratios in the morning at western and southern Basin sites and determine the extent to which this ratio affects the maximum ozone levels at the eastern and northern Basin sites. Recalculate  $\text{ROG}/\text{NO}_x$  ratios for specific reactivity classes, especially aromatics, and examine receptor area ozone concentrations for cases of high and low ratios in the source areas. Examine the emissions maps to compare the quantity of fresh hydrocarbon and  $\text{NO}_x$  injected along the trajectories, and determine the degree to which this might interfere with the conclusions drawn from  $\text{ROG}/\text{NO}_x$  ratios in the source areas.

Examine aircraft traverses and compare ozone,  $\text{NO}_x$ , and hydrocarbon concentrations to simple equilibrium calculations similar to those of Calvert (1976a, 1976b). Examine nighttime concentrations of  $\text{O}_3$  and precursors above the inversion and off the coastline to determine the degree of carryover from the previous day. Compare  $\text{ROG}/\text{NO}_x$  ratios with those calculated from localized emissions grid squares near the western and southern sites; identify potential causes of the discrepancy. If documentable day-to-day changes in emissions patterns (temporal and spatial) occur, compare the oxidant and hydrocarbon concentrations among otherwise similar meteorological conditions (e.g. Davidson and Cassmassi, 1985). Compare oxidant values in cases with high ambient aromatic hydrocarbon concentrations to values obtained when aromatic hydrocarbon concentrations are low.

Project 3.4: Case Studies on Aerosol Sulfate, Nitrate, and Carbon Formation. Calculate equilibrium concentrations for sulfur, nitrogenous, and organic species in the gas and particle phases for each sampling site and time and compare with the aerosol measurements. Examine fine and coarse particle chemical compositions, and infer the compounds which are present. Verify these inferences via single particle analysis of selected filter samples and determine the extent to which the aerosol is internally or externally mixed. Stratify ground-based and airborne measurements by day and night and compare chemically speciated size distributions and their changes with respect to time, thereby testing the hypotheses of Richards (1983). Examine speciated particulate and gaseous concentrations of organic compounds to estimate the fractions of organic carbon which are of primary and secondary origins. Coordinate with Projects 2.1 and 2.2 to perform this primary/secondary attribution of organic carbon.

#### **6.4.4 Objective 4: Dependence of Pollutant Spatial Distributions on Emission Height and Meteorology**

Project 4.1: Case Studies of Natural and Injected Tracer Data. Examine the results of Projects 2.1 and 2.2 to differentiate between the primary emissions from elevated and ground level source at near-source and far-source receptors. Compare these estimates with the concentrations of perfluorocarbons and  $\text{SF}_6$  injected at high and low elevations. Examine the vertical concentrations above ground stations to determine gradients which might be caused by elevated source emissions, and determine which sources might be the cause from the elevated emissions maps produced in Project 1.1. Examine aircraft measurements above sampling sites along well-defined trajectories between source and receptors to determine the travel time required for vertical mixing of elevated source emissions. Stratify this travel time by atmospheric stability categories, and identify significant differences. Estimate the quantity of ozone,  $\text{NO}_x$ , particulate matter, and hydrocarbons which are contributed to surface concentrations by mixing as the inversion rises; and estimate the vertical distance for which vertical homogeneity is achieved as a function of time of day. Compare the results of this analysis with the assumptions of source models, and determine those cases for which the model assumptions would be valid. Examine speciated hydrocarbon and CO concentrations during high and low temperature periods to infer higher or lower evaporative fuel emissions as a function of temperature; normalizing hydrocarbon species with respect to CO may minimize the effects of different weather conditions on absolute hydrocarbon levels.